

CURABLE POLYBUTADIENE-BASED RESINS HAVING IMPROVED PROPERTIES

This application is a continuation of co-pending patent application Ser. No. 64,170, filed Aug. 6, 1979, which is a continuation of Ser. No. 813,207, filed July 5, 1977, now abandoned, which is in turn a continuation-in-part of patent application Ser. No. 546,250, filed Feb. 3, 1975, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to certain polybutadiene-based resins, curable by peroxy initiation, and having improved thermal, impact, and cure-through-volume properties. More specifically, it relates to resins which may be viewed as a reaction product of, e.g., polybutadiene diols and their acrylonitrile copolymers with, e.g., methacrylate-capped aromatic diisocyanates.

2. Prior Art

It is known that curable resins having desirable properties may be prepared as the reaction product of an organic polyisocyanate and an acrylate ester having an active hydrogen in the non-acrylate portion of the ester. Such resins are disclosed in U.S. Pat. No. 3,425,988 to Gorman et al. This patent relates specifically to monofunctional, acrylate-terminated material which is reacted with organic polyisocyanate in such proportions as to convert all of the isocyanate groups to urethane or ureide groups. The acrylate esters are preferably the acrylates and methacrylates containing hydroxy or amino functional groups on the non-acrylate portions thereof.

U.S. Pat. No. 3,678,014 to Suzuki et al. discloses a peroxide-curable thermosetting resin comprising a reaction product of a polybutadiene or copolybutadiene having a preponderance of the 1,2-configuration of butadiene units and terminated with hydroxyl or carboxyl groups, and an isocyanate compound obtained by the reaction of an organic polyisocyanate with an olefinic compound such as a hydroxyalkyl acrylate or hydroxyalkyl methacrylate. The resins so produced are curable with peroxy initiators and are said to be useful as coatings or adhesives. Such resins are not fully satisfactory in terms of various properties, such as impact strength, thermal strength (i.e., strength at high temperatures or after high-temperature aging), and, moreover, do not have the ability to cure satisfactorily through relatively large gaps, e.g., approximately 40-50 mils or more.

U.S. Pat. No. 3,674,743 to Verdol et al. tracks self-curing solid elastomers made by reacting a polyfunctional, hydroxyl-reactive compound (e.g., a polyisocyanate) with a polyhydroxyl polymer. That polymer is made from a 1,3-diene having about 40-70 percent trans-1,4-unsaturation and about 10-30 percent cis-1,4-unsaturation. The elastomeric product is useful as a binder, coating, etc., and is stated to have certain improved properties, e.g., flexibility and tear strength. However, the product is not known as an adhesive, no thermal or cure-through-gap properties are suggested, and no particular advantage is attributed to the 1,4-unsaturation. Moreover, the product is not acrylate/methacrylate-terminated and thus is fundamentally different in structure from the compounds of the present invention.

U.S. Pat. No. 3,431,235 to Lubewitz discloses the cyclization of a reaction product of, e.g., hydroxyl-terminated 1,2-polybutadiene with toluene diisocyanate. While this results in certain useful properties, the heat stability, cure speed, and cure-through-volume properties are unsatisfactory.

SUMMARY OF THE INVENTION

Now, however, there is provided a polymerizable adhesive and sealant composition having improved thermal and impact properties and curable through gaps of more than 40 mils, comprising:

I. a polymerizable product corresponding in structure to a reaction product of:

(a) a polybutadiene polyol or polyamine comprising about 5 to about 150 butadiene units and having at least about 70 percent of the butadiene units in the 1,4-configuration and selected from the group consisting of polybutadiene and butadiene acrylonitrile copolymers, and either of:

(b) (i) a molar excess of a reaction product of: a molar excess of an aromatic or cycloaliphatic polyisocyanate with a compound selected from the group consisting of an aromatic or cycloaliphatic polyol, or

(ii) a molar excess of an aromatic or cycloaliphatic polyisocyanate,

the product of (a) and (b)(i) or (a) and (b)(ii) subsequently being reacted with a molar excess of a hydroxyalkyl acrylate, a hydroxyalkyl methacrylate, an aminoalkyl acrylate, or an aminoalkyl methacrylate; and

II. A free radical initiator.

There is also provided a process for preparing the monomer of Part I, above, comprising reacting the polybutadiene of part I(a) with either of:

(i) a molar excess of a reaction product of: a molar excess of an aromatic or cycloaliphatic polyisocyanate with a compound selected from the group consisting of an aromatic or cycloaliphatic polyol, or

(ii) a molar excess of an aromatic or cycloaliphatic polyisocyanate,

the product subsequently being reacted with a molar excess of a hydroxyalkyl acrylate, a hydroxyalkyl methacrylate, an aminoalkyl acrylate, or an aminoalkyl methacrylate.

In addition, there is provided a process for sealing or adhering surfaces which comprises applying to at least one of said surfaces the above polymerizable compositions, then placing said surfaces in an abutting relationship until the composition has cured.

DETAILED DESCRIPTION OF THE INVENTION

The monomer of the present invention may be viewed as a one-component polymerizable block copolymer having rigid and flexible segments. This is achieved by the chemical linking of two "pre-polymers" which are subsequently "capped" with acrylate, e.g. methacrylate, functionality. Accordingly, in a preferred embodiment, a "flexible" polymeric butadiene polyol segment of relatively low molecular weight is reacted with a molar excess of a "rigid" diisocyanate such as toluene diisocyanate or methylene diisocyanate (4,4'-ddiisocyanato diphenylmethane), thereby forming urethane linkages. Before reacting with the polybutadiene polyol, the diisocyanate is preferable reacted in excess with another rigid moiety containing at least two